

## CHARACTERISTICS OF INLAND ACID SULFATE SOILS OF THE LOWER MURRAY FLOODPLAINS, SOUTH AUSTRALIA

Luke Wallace<sup>1</sup>, S.A. Welch<sup>1,2</sup>, Dirk Kirste<sup>1</sup>, Sara Beavis<sup>3</sup> & D.C. McPhail<sup>1</sup>

<sup>1</sup>CRC LEME, Department of Earth and Marine Sciences, Australian National University, Canberra, ACT, 0200

<sup>2</sup>CRC LEME, Research School of Earth Sciences, Australian National University, Canberra, ACT, 0200

<sup>3</sup>CRC LEME, Centre for Resource and Environmental Studies, Australian National University, Canberra, ACT, 0200

### INTRODUCTION

Significant accumulations of sulfidic materials are common in coastal environments due to: (1) available sulfur from ocean waters; and, (2) bio-mediated sulfate reduction (Dent & Pons 1995, Lin *et al.* 1995). It has now become evident that significant deposits of sulfides can also form in saline inland landscapes (Fitzpatrick *et al.* 1996). The low solubility of sulfides under reducing conditions leads to sulfide accumulation (Berner 1978). Sulfides remain relatively benign under reducing conditions but, in high concentrations (> 0.06 wt. %, trigger value), sulfide oxidation can directly harm natural ecosystems through acidification, deoxygenation, element mobilisation and noxious gas emissions (Sammut & Lines-Kelly, 1996). Although these effects are well documented for coastal systems (Ward *et al.* 2004), the extent to which they may occur in inland sulfidic sediments is not yet fully understood.

Salinity impacts an estimated 25% of the Lower Murray floodplains area and is expected to double over the next 50 years (Lovering *et al.* 1998). A recent survey of the Lower Murray found environmentally significant sulfide concentrations within wetlands and saline disposal basins such as the Loveday Disposal Basin (Lamontagne *et al.* 2004). The Loveday Disposal Basin is a terminal basin that has received saline groundwater and irrigation discharge for 30 years. With little output of salts the Basin has become hypersaline and is now undergoing remediation. As the remediation of salinity may expose sulfidic sediments to the atmosphere, the benefits of draining saline waters may be counteracted by sulfide oxidation (Lamontagne *et al.* 2004). Currently little is known about these sulfidic sediments or what environmental threats they may pose if disturbed. To understand and manage these environments the fundamental processes and mechanisms that drive sulfur cycling in the floodplains of the Lower Murray need to be elucidated. Loveday is currently being used as a test site for management of sulfidic sediments in the Lower Murray (Lamontagne *et al.* 2005) and will be used as a case study for sulfur cycling in the Lower Murray floodplains for this project.

### METHODS

Waters were measured for physiochemical parameters in the field and analysed for cations via Inductively Coupled Plasma-Atomic Emission Spectrophotometry (ICP-AES) and anions by Ion Chromatography (IC). Sediments were analysed for mineral composition and bulk chemistry by X-ray diffraction, X-ray fluorescence and scanning electron microscopy, whilst the sulfur fractions were determined gravimetrically by LECO, chromium-reducible-sulfur and acid-volatile-sulfur. Sulfidic sediments were oxidised in the laboratory under atmospheric conditions and with hydrogen peroxide to assess oxidation processes and acid production potential.

### RESULTS

#### Basin Sediments

The Loveday Basin contains approximately 1-2 m of low permeability wetland clays underlain by permeable sands and silts. Below 0.4 m depth the wetland clays are largely homogenous throughout the Basin and are comprised of kaolinite, illite and smectite with quartz silt horizons. The mineralogy and textures of the wetland clays above 0.4 m are highly variable with high salinity, cracked sediments and abundant root channels. Basin-wide these upper wetland clays demonstrate three principal zones that change with height above the water table: 1) the 'Dry Zone' clays are mottled with iron oxides and covered in centimetres of salt crust; 2) the clays of the 'Wet-Dry Zone' are also mottled with iron oxides and form prominent pedes covered in sulfidic black ooze during wetting and salt crust during drying; and, 3) the 'Wet Zone Clays' have a permanent water cover and contain minor iron oxide mottling with a surface coating of sulfidic black ooze.

#### Sulfur Form, Amount and Distribution

Sulfate is concentrated in the upper sediments of the Basin dissolved in waters as sulfate (up to 8,700 mg/l) and precipitated as gypsum in salt efflorescence (up to 10 wt. %). Reduced sulfur species monosulfides and pyrite are largely restricted to these more saline upper sediments averaging 0.05 wt. % and 0.5 wt. % respectively. Jarosite (which forms at pH < 4) is also common in small amounts associated with high pyrite

concentrations and oxidising conditions. The estimated amount of sulfur stored in the Basin waters and sediments to depth of 2.5 m is approximately 40,000 tons, 63% of which is stored above 0.4 m depth.

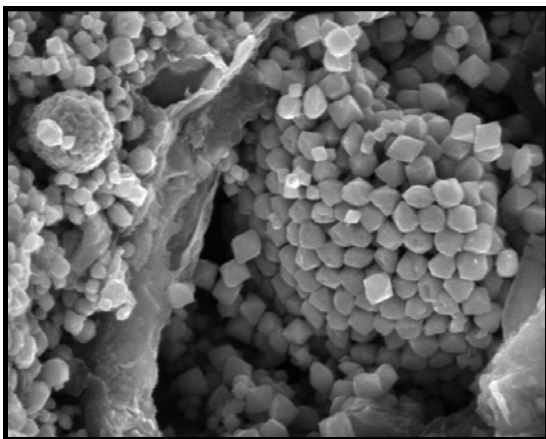
The distribution of sulfur bearing minerals in the upper 0.4 m of sediments is not uniform but highly heterogeneous with prominent peds and abundant root channels (Figure 1). Gypsum not only increases concentration up-profile but also towards sediment cracks and the exterior of peds. Monosulfides are largely restricted to the black ooze which coats the benthos around peds and forms within sediment cracks. Pyrite framboids are concentrated around plant roots (Figure 2, 1.0 wt. %) and within micro-pores but have much lower concentrations around sediment cracks with iron oxide mottles (0.1 wt. %). These characteristics result in a complex network of sulfur bearing minerals in the upper sediments.



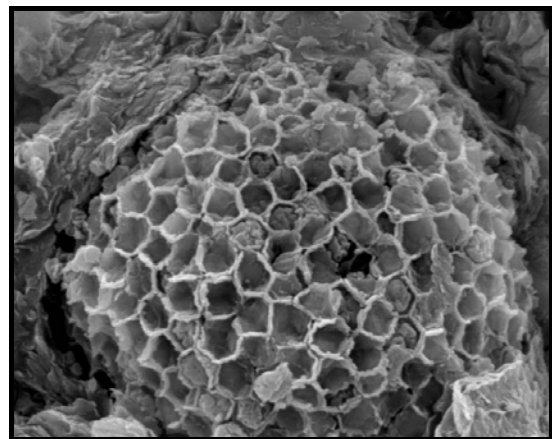
**Figure 1:** Sediments of the Loveday Basin (2005) with prominent peds and surface remains of wetland plants (left) which have left abundant root channels in the upper sediments.

#### Acidification

The sediments of the Loveday Basin have predominantly neutral pH, although, some sites have become acidic (pH 3.2) upon oxidation. Acidification is restricted to sulfidic horizons (above 0.4 m) where the neutralising capacity of the sediments has been exceeded. Carbonates are concentrated with salt efflorescence in the upper 0.05 m of sediments and along sediment cracks. Where the distribution of sulfides does not match that of the carbonates, acidification is marked by the formation of jarosite along cracks and old root channels. Jarosite is also found in neutral sediments as micro-coatings around pyrite crystals (Figure 3). The presence of jarosite indicates acid micro-environments form in neutral sediments during pyrite oxidation.



**Figure 2** Pyrite framboids surrounding plant root.



**Figure 3** Jarosite network surrounding pyrite framboid

#### DISCUSSION

The Loveday Basin has received sulfur from groundwater and irrigation discharge. Concentrated by evaporation near surface, sulfur is present as dissolved sulfate and gypsum but also as sulfides and jarosite above 0.4 m depth. As the outputs of sulfur from the Basin have been relatively small the sulfur that has entered the Basin has been trapped. Preliminary estimates show the Basin could contain up to 40,000 tons of

sulfur to 2.5 m depth.

The sulfur-rich surface sediments are not uniform but highly irregular with prominent cracks and abundant plant roots. These preferential flow paths may act as conduits for both saline waters and atmospheric oxygen resulting in the formation and oxidation of sulfur bearing minerals. The resulting heterogeneous distribution of sulfur minerals within surface sediments will require detailed sampling to give a more robust estimate of Basin sulfur stores.

Although the majority of the Loveday sediments have neutral pH, some sulfidic horizons have become acidic upon oxidation. Acidification is restricted to sulfidic sediments between 0.05 and 0.4 m depth and is typically associated with jarosite in cracks and root channels. Jarosite is also present in neutral pH sediments closely associated with pyrite in acidic micro-environments. These observations show that pyrite oxidation and acidification occurs over a range of spatial scales. Like sulfur distribution, the acidification of Basin sediments is not homogeneous and further investigation will be required to quantify the potential for acid production.

### **FUTURE WORK**

This project is focused on the cycling of sulfur through the sulfidic sediments of the Lower Murray floodplains. Future work will include detailed analysis of sulfur species in sediments, waters and gasses of the Loveday Basin. Sediments will be investigated under both field and laboratory conditions to determine the processes and rates of sulfur oxidation and reduction. The outcome of this project is to develop a conceptual model to better understand and manage sulfidic sediments in inland environments.

### **References**

- BERNER R.A. 1978. Rate Control of Mineral Dissolution under Earth Surface Conditions. *American Journal of Science* **278(9)**, 1235-1252.
- DENT D.L. & PONS L.J. 1995. A world perspective on acid sulphate soils. *Geoderma* **67(3-4)**, 263-276.
- FITZPATRICK R.W., FRITSCH E. & SELF P.G. 1996. Interpretation of soil features produced by ancient and modern processes in degraded landscapes: V. Development of saline sulfidic features in non-tidal seepage areas. *Geoderma* **69(1-2)**, 1-29.
- LAMONTAGNE S., HICKS W., FITZPATRICK R.W. & ROGERS S. 2004. Survey and description of sulfidic materials in wetlands of the Lower River Murray floodplains: Implications for floodplain salinity management. *CRC LEME Open File Report 165 (CSIRO Report 18/04)*.
- LAMONTAGNE S., HICKS W., ROGERS S. & FITZPATRICK R.W. 2005. Management of sulfidic materials in disposal basins: the Loveday Swamp case study. In: ROACH I.C. ed. *Regolith 2005 – Ten Years of CRC LEME*. CRC LEME, pp. 179-182.
- LIN C., MELVILLE M.D. & HAFER S. 1995. Acid sulphate soil-landscape relationships in an undrained, tide-dominated estuarine floodplain, Eastern Australia. *Catena* **24(3)**, 177-194.
- LOVERING J.F., CRABB P. & EVANS R. 1998. Salinity in the Murray-Darling Basin: a critical challenge for the 21st Century. *International groundwater conference*.
- SAMMUT J. & LINES-KELLY R. 1996. *An introduction to acid sulfate soils*. Environment Australia and Agriculture, Fisheries and Forestry - Australia, ISBN 0 7347 1208 1. Available online at <http://www.deh.gov.au/coasts/cass/pubs/acidsulfate.pdf>.
- WARD N.J., SULLIVAN L.A., FYFE D.M., BUSH R.T. & FERGUSON A.J.P. 2004. The process of sulfide oxidation in some acid sulfate soil materials. *Australian Journal of Soil Research* **42(4)**, 449-458.